



Magnetic Hardening Induced by Nonmagnetic Organic Molecules

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We reveal for the first time through a theoretical first-principles study that the adsorption of a nonmagnetic π -conjugated organic molecule on a ferromagnetic surface locally increases the strength of the magnetic exchange interaction between the magnetic atoms binding directly to the molecule. This magnetic hardening effect leads to the creation of a local molecular mediated magnetic unit with a stable magnetization direction and an enhanced barrier for the magnetization switching as compared to the clean surface. Remarkably, such a hybrid organic-ferromagnetic system exhibits also a spin-filter functionality with sharp spin-split molecularlike electronic features at the molecular site.

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In molecular electronics [1], organic molecules are already employed in technologically relevant devices like single molecule diodes [2–4] or organic field-effect transistors [5,6]. Such electronic devices rely on the manipulation of the molecular electronic structure due to the molecule-surface interaction; i.e., it involves the tuning of the hybrid molecule-substrate electronic properties related to electron charge degree of freedom.

A next technological relevant step is to tailor the electronic structure of the molecular devices with respect to electron spin degree of freedom. Indeed, the emerging field of molecular spintronics [7,8] highlighted the possibility of experimentally integrating single molecule magnets (SMMs) [9] in a supramolecular spin-valve device [10]. Also the transport mechanism for SMMs in a molecular junction was recently investigated [11,12]. Furthermore, in a recent experimental study of a double-decker molecule (TbPc_2) on a ferromagnetic surface [13], it was suggested that the magnetic exchange coupling parameters describing the molecule-substrate magnetic interaction can vary depending on the amount of charge density transferred at the molecule-surface interface. Another possible use of molecules in spintronic devices is to employ them as spin filters as shown in experimental as well as in theoretical studies [14–16].

In this Letter, we explore the possibility of constructing a spintronic device starting from a ferromagnetic surface by locally embedding magnetic units created after the adsorption of a nonmagnetic organic molecule, which also exhibits a spin-filter functionality with sharp molecularlike electronic features at the molecular site. Ideally, this molecule should be chemisorbed on the magnetic substrate such that the molecule-metal interaction can locally modify the magnetic properties of the magnetic surface atoms leading to an organic-based magnetic unit [8]. The challenge imposed by such a hybrid organic-magnetic system is to recognize that an organic molecule chemisorbed on a magnetic surface forms near the Fermi energy broad hybrid

molecule-surface bands which, however, can be locally spin unbalanced [17]. In contrast, a well defined spin-filter functionality requires sharp molecularlike electronic states [18], which can be obtained in the case of a physisorbed molecule [8]. To reconcile these two contradicting requirements, we theoretically advocate nonmagnetic organic molecules with a biplanar structure of π -conjugated carbon bonds chemisorbed on a magnetic substrate where both (1) a local molecular-based magnetic unit is formed and (2) a spin-splitting of sharp molecularlike features is also present. As a proof of principle, the adsorption of a single 2,2-paracyclophane (PCP) molecule with the chemical formula $\text{C}_{16}\text{H}_{16}$ on a magnetic Fe/W(110) substrate is a specific example where both effects are found. Importantly, these magnetic features can be generalized for other similar molecules since PCP is a prototype for a wide class of layered π -conjugated molecular structures. We note in passing that one monolayer (1 ML) of Fe on W(110) exhibits ferromagnetism with an in-plane magnetization direction [19] and is a substrate of choice to perform, for instance, spin-polarized scanning tunneling microscopy (STM) experiments [14,20].

The key molecular feature of the PCP molecule is a biplanar (columnar) π -conjugated electronic structure that forms a 3D π -aromatic network. Thus, it chemisorbs with the lower benzenelike ring on the magnetic surface leading to an enhancement of the exchange interaction between the Fe atoms underneath the molecule (local magnetic hardening) with respect to that of the clean Fe surface atoms. Additionally, as a direct consequence of this three-dimensional π character of the PCP molecule, the sharp electronic states are spin-split at the upper molecular ring. Therefore, the PCP molecule together with hybridized Fe atoms underneath can be considered as a magnetic unit whose enhanced barrier for the magnetization switching induced by large coercivity fields and spin-dependent filtering properties can be of technological interest for molecular memory spintronic devices [8].

Our theoretical study has been carried out by performing first-principles spin-polarized calculations in the framework of the density functional theory (DFT) [21,22] as implemented in the VASP code [23,24]. In our simulations we employed pseudopotentials generated with the projector augmented plane-wave (PAW) method [25] using the Perdew-Burke-Ernzerhof formulation [26] for the exchange-correlation functional. The plane wave cutoff energy was set to 500 eV throughout our *ab initio* calculations. The PCP-Fe/W(110) system has been modeled by a (4×5) supercell consisting of 40 Fe or W atoms in the surface unit cell and of a 6 layers W slab covered with one layer of Fe and a single PCP molecule adsorbed on one side of the slab [27].

As depicted in Fig. 1, in the ground-state geometry, a single PCP molecule adsorbs on the ferromagnetic Fe/W(110) substrate with the lower benzenelike ring on top of a surface hollow site such that two C atoms are directly above the Fe ones (denoted as Fe1) and two C=C double bonds are on top of two other Fe atoms (denoted as Fe2). It is important to note that PCP is chemisorbed on this magnetic substrate via its lower ring with an adsorption distance of 1.95 Å and the corresponding adsorption energy is $E^{\text{ads}} = -2.457$ eV [28].

As already mentioned in the introductory portion of this Letter, a basic feature of the PCP molecule is its biplanar π -conjugated electronic structure, which allows one 6π aromatic ring to be in direct contact with the substrate while the other 6π aromatic ring is at the vacuum interface. Since the upper ring is connected to the lower one through two sp^3 -hybridized carbon atoms, the molecule-surface interaction can lead to electronic states with a different

character on these rings: broad hybrid molecular-metal bands at the lower ring and sharp spin-polarized electronic states at the upper one.

Indeed, a strong interaction between the PCP molecule and the Fe/W(110) surface as suggested by the calculated adsorption energy is confirmed by the analysis of the projected density of states (PDOS) depicted in Fig. 2(a). At the molecular site, one can observe that the PDOS of the lower ring consists of broad σ and π features due to a strong hybridization mainly with the substrate's d states. This broadening of the molecular electronic states of the lower ring is typical for chemisorption and leads to a strong change of the electronic and magnetic properties of the iron atoms binding the carbon atoms of the molecule. More specifically, the magnetic moment of the Fe1 atoms binding directly the C atoms of the molecule is $\approx 2.09\mu_B$ and $\approx 2.32\mu_B$ for Fe2 atoms, being smaller than the magnetic moment ($\approx 2.48\mu_B$) of the Fe surface atoms situated more distant from the molecule, which is practically identical with the magnetic moment of the Fe atoms of the clean surface. This difference between the magnetic moments of the Fe1 and Fe2 atoms is related to slightly different Fe1—C (2.06 Å) and Fe2—C (2.24 Å) bond distances, which in turn lead to slightly different hybridizations between these atoms and the PCP molecule.

Since, upon adsorption, the lower PCP ring interacts directly with the four Fe atoms underneath the molecule (Fe1 and Fe2), we have also considered the possibility that the magnetic moments of some of these four Fe atoms were antiferromagnetically (AFM) oriented with respect to the rest of the surface. Calculating several AFM configurations with only two Fe1, only two Fe2, or all four Fe1 and Fe2 atoms AFM coupled to the rest of the Fe atoms, we evaluated the exchange constants J describing the coupling strength of the Fe—Fe magnetic interactions applying a Heisenberg model with an Hamiltonian $\mathcal{H} = -\sum_{i>j} J_{ij} \mathbf{S}_i \mathbf{S}_j$. Then, the energy difference per Fe atom between the ferromagnetically and

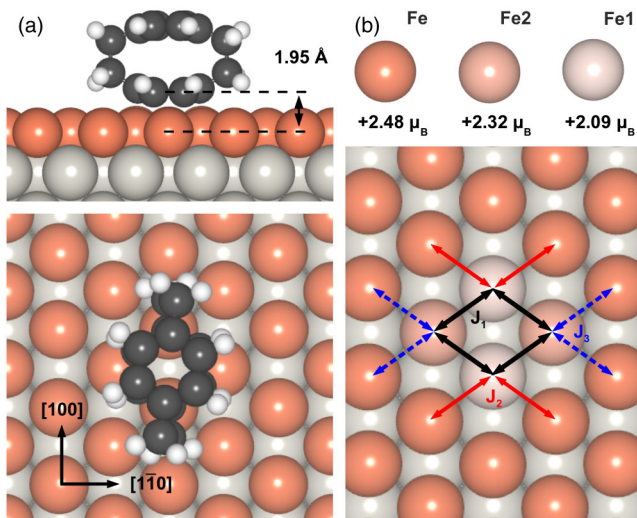


FIG. 1 (color online). (a) The side and top view of the hollow site ground-state adsorption geometry of a single PCP molecule on the ferromagnetic Fe/W(110) surface. (b) Top view and magnetic moments of the clean Fe surface atom and the four Fe atoms [34] that chemically interact with the lower ring of the PCP molecule.

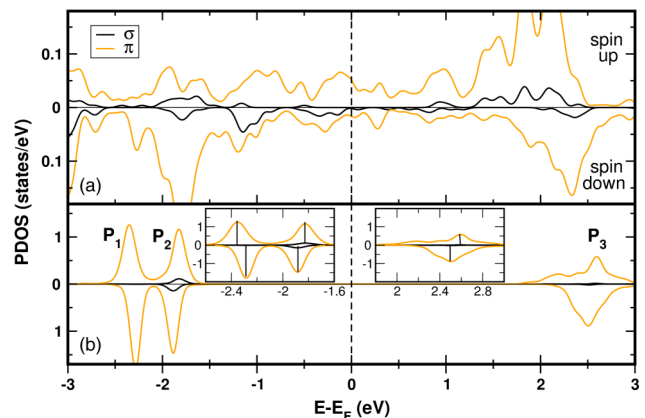


FIG. 2 (color online). The PDOS at the molecular site expressed in terms of the σ and π type molecularlike orbitals of the lower (a) and the upper (b) ring of the PCP molecule on the Fe/W(110) surface [35].

antiferromagnetically coupled system is given by $E_{\text{FM}} - E_{\text{AFM}} = -2N_n J_{ij} m_i m_j$ where m_i and m_j are the magnetic moments of the interacting Fe atoms at the surface and $N_n = 4$ is the number of nearest neighbor Fe atoms. We arrive at the following values for the exchange couplings between various nearest Fe neighbors (in units of meV/μ_B^2): $J_1 = 15.65$, $J_2 = 5.84$, and $J_3 = 5.17$, while the exchange coupling of the clean Fe surface is $J_S = 5.42$.

A key result of our study is that the value of J_1 describing the magnetic interactions between the Fe atoms underneath the PCP molecule is significantly larger than that for the clean surface atoms. As a consequence, the PCP and the four Fe atoms directly underneath can be regarded as a local molecular-based magnetic unit embedded within the ferromagnetic surface. It is also important to note that, for this hybrid system, the J_2 and J_3 between the Fe atoms underneath the molecular unit and the neighboring atoms are slightly larger and slightly smaller than J_S , which reveals the locality of the magnetic hardening and a complex magnetic interaction pattern between the local PCP-based magnetic unit and the surrounding ferromagnetic surface atoms. Interestingly, this behavior is opposite to that unveiled for another π molecular-based magnetic unit on a Co surface [8], where a strong decoupling of the molecular magnetic unit with respect to the magnetic substrate took place.

The magnetic hardening mechanism responsible for the enhanced magnetic interactions between the Fe atoms of the local molecular-based magnetic unit with respect to those of the clean surface can be inferred from the analysis of the PDOS of the d states for the FM configuration shown in Fig. 3. One can observe that with respect to the total d PDOS of the Fe atoms of the clean surface, the PDOS of the Fe1 and Fe2 atoms underneath the PCP molecule shows significant differences over a large energy interval around the Fermi energy. Importantly, these differences in PDOS

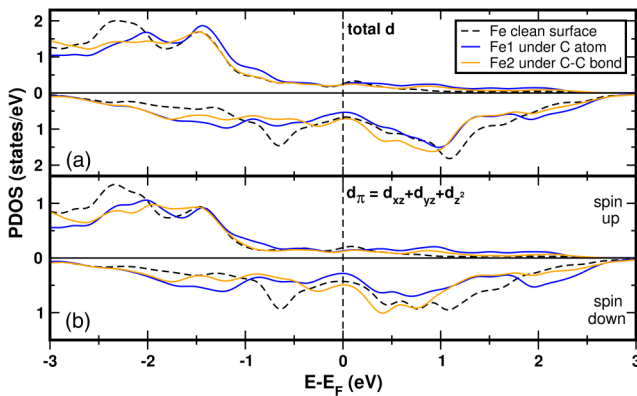


FIG. 3 (color online). The total d - (a) and the out-of-plane d_π - (b) PDOS for an Fe atom of the clean surface and for the Fe1 and Fe2 atoms underneath the PCP molecule when all iron atoms are in the ferromagnetic (FM) configuration. Note that $d_\pi = d_{xz} + d_{yz} + d_{z^2}$.

can be traced back to a strong hybridization of the out-of-plane d_π ($d_\pi = d_{xz} + d_{yz} + d_{z^2}$) states of each Fe1 and Fe2 with the π -like molecular ones. This observation also implies that the d_π states of the Fe1 and Fe2 atoms become strongly coupled via the π molecular orbitals since they contribute to common hybrid $\pi - d_\pi$ orbitals. Therefore, an enhanced exchange coupling J_1 between the Fe1 and Fe2 atoms in the FM configuration is mainly due to the hybridization of the Fe1 and Fe2 out-of-plane d_π with the π system of the PCP molecule similar to the general indirect exchange mechanism [29]. Furthermore, for the surface Fe1 and Fe2 atoms, this tuning mechanism does not lead to a significant change of the J_2 and J_3 exchange couplings as compared to the one based on the molecule-surface charge transfer mentioned in [8], that revealed a large softening of the corresponding exchange parameters.

Concerning the magnetic properties of this hybrid system, a further crucial point of investigation is if and how locally the magnetization direction of the Fe/W(110) surface changes upon adsorption of the PCP molecule. To scrutinize this issue, we included in our spin-polarized *ab initio* calculations the spin-orbit coupling to evaluate the magnetocrystalline anisotropy energy (MAE), which determines the orientation of the magnetization (aside from the shape anisotropy, that is a tiny quantity in this system), i.e., whether the easy axis of the magnetization is in the surface plane (along the $[1\bar{1}0]$ or $[100]$ direction) or out-of-plane (along the $[110]$ axis). As reported in Table I, for the PCP-4Fe magnetic unit embedded within the Fe/W(110) surface we obtained a difference in MAE of 6.71 meV between the in-plane easy axis corresponding to the $[1\bar{1}0]$ direction and the hard axis $[100]$. Note that, for the clean Fe/W(110) surface, our PAW calculations lead to a MAE value of 2.92 meV/(Fe atom) which is very close to the value of 2.79 meV/(Fe atom) obtained with the full-potential linear augmented plane wave method [19]. Therefore, the important outcome of the MAE calculations is that the PCP-Fe/W(110) system has the same easy axis, as that of the clean surface, but is more stable.

To explore the consequences of the strong impact of the hybrid organic-metallic states formed at the interface on the macroscopic magnetic properties of the hybrid system, we performed simulations for a magnetization reversal

TABLE I. The different nearest-neighbor magnetic exchange coupling strengths, J , between Fe atoms as indicated in Fig. 1(b), the MAE, and the spin-splitting of the $P1$, $P2$, and $P3$ PDOS peaks (see Fig. 2) for the PCP molecule adsorbed on 1 ML Fe on the W(110) surface. The easy axis of the magnetization $[[1\bar{1}0]$ axis in Fig. 1(a)] of the PCP-4Fe magnetic unit embedded within the Fe/W(110) surface is indicated by a MAE of 0.00 meV.

J (meV/μ_B^2)				MAE ($\text{meV}/\text{PCP-4Fe}$)			Spin splitting (meV)		
	J_1	J_2	J_3	$[1\bar{1}0]$	$[100]$	$[110]$	$P1$	$P2$	$P3$
	15.65	5.84	5.17	0.00	6.71	5.35	65	57	88

process at finite temperature using the Monte Carlo (MC) method [30] (see also Supplemental Material [31]). In order to clearly illustrate the magnetic hardening effect induced by the adsorbed PCP molecule, in our MC calculations the PCP-1 ML Fe/W(110) system was modeled at a higher coverage than in DFT calculations. More specifically, the MC cell contains 24 Fe atoms instead of 40 Fe atoms as used in the DFT simulations. It corresponds to a coverage density of $4/24$, where four denotes the number of Fe atoms directly interacting with the PCP molecule [two Fe1 and two Fe2, see Fig. 1(b)] while twenty-four corresponds to the total number of surface Fe atoms.

As depicted in Fig. 4(a), at a fixed temperature the simulated magnetization curves provide an estimate of the coercivity field H_c required to switch the magnetization of the molecule-surface system. Furthermore, the H_c evaluated from the magnetization curves obtained at different temperatures exhibits a linear dependence for both clean Fe/W(110) and PCP-Fe/W(110) systems [see Fig. 4(b)]. The most important outcomes of the MC investigations are the increase of the Curie temperature by 27 K and the large increase of the coercivity field ΔH_c of up to ~ 4 T for the PCP-covered Fe/W(110) surface relative to the uncovered one. The difference of the latter becomes even larger as the temperature decreases. Besides this, by increasing the coverage the ΔH_c increases further, e.g., for a higher coverage of $4/12$, the ΔH_c is almost twice as large as at half coverage of $4/24$. Therefore, these MC results clearly demonstrate the ability of PCP molecules to locally increase the barrier for domain nucleation of the hybrid organic-ferromagnetic system, which in turn can be used to increase the Curie

temperature (see also Supplemental Material [31]) or to specifically pattern magnetic areas and use them as magnetic storage units.

Finally, as an additional remarkable feature, it is important to note that the PDOS of the upper π ring atoms at the vacuum interface shown in Fig. 2(b) presents sharp molecularlike features at -2.3 eV (denoted as $P1$) and at -1.8 eV (denoted as $P2$) for the occupied states and at 2.5 eV (denoted as $P3$) for the unoccupied ones. The most important characteristic displayed by the PDOS is that the spin degeneracy of these molecular orbitals for the PCP molecule in the gas phase is lifted due to the interaction with the magnetic surface leading to an exchange splitting between the majority and the minority states for the $P1$ peak of 65 meV, 57 meV for the occupied $P2$ peak, and an exchange splitting of 88 meV for the unoccupied $P3$ one at 2.5 eV. This implies that the nonmagnetic PCP molecule adsorbed on the ferromagnetic Fe/W(110) surface [32] acts as a molecular spin filter [14,20] although after adsorption the molecule remains nonmagnetic. An important consequence of this behavior is that, depending on the applied bias voltage, different spin polarization [33] of the upper π ring can be accessed in an STM experiment depending on how many spin up and down peaks are in that specific measured energy interval [18].

In conclusion, our spin-polarized first-principles study demonstrated the possibility of designing a hybrid organic-ferromagnet interface system consisting of a nonmagnetic organic molecule (PCP) chemisorbed on a magnetic substrate [Fe/W(110)], which (i) all-in-all acts as a local embedded molecular-based magnetic unit due to a magnetic hardening of the substrate and (ii) simultaneously exhibits a spin-filter functionality with sharp spin-split molecularlike electronic features at the molecular site, previously known only for physisorbed molecules. This molecular induced local magnetic hardening is a result of the hybridization between the π -molecular orbitals of the lower PCP ring with the d states of the magnetic interface that leads to increased exchange interactions and a larger magnetic anisotropy energy, which results in a stable magnetization axis, an increase of the Curie temperature as well as of the magnetic coercivity fields. In practice, such molecular-based magnetic units can play an important role for memory device applications. We conjecture that the potentially important technological devicelike characteristics (i) and (ii) are generic to molecules with a biplanar structure of π -conjugated carbon bonds, which allows chemisorption on magnetic surfaces and having molecular-type spin-split electronic states of π orbitals at a larger distance from the interface.

The computations were performed under the auspices of the VSR at the computer JUROPA and the GCS at the high-performance computer JUQUEEN operated by the JSC at the Forschungszentrum Jülich.

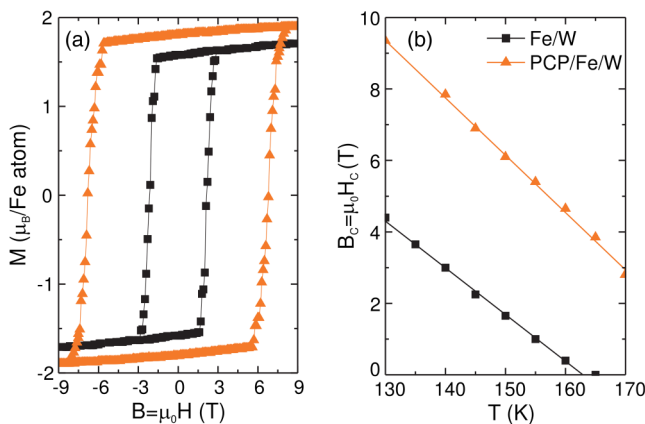


FIG. 4 (color online). Results of the Monte Carlo simulations (a) for the magnetization-reversal process at $T = 145$ K and (b) for the coercivity field H_c below ordering temperature for a clean (squares) and PCP covered (triangles) magnetic Fe monolayer. Solid lines in (b) result from a linear fit of the H_c as a function of temperature. The Curie temperatures are $T_C = 165$ K and $T_C = 192$ K for the clean and PCP-covered Fe/W(110) surface, respectively.

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- [32] It is worth noting that a similar spin-split of the hybrid molecule-surface electronic states at the upper PCP ring is obtained when the molecule is adsorbed on a ferromagnetic 2 ML Fe/W(110) surface which contrary to 1 ML Fe/W(110) has an out-of-plane easy axis.
- [33] The spin polarization is defined as the ratio $(n^{\text{up}} - n^{\text{dn}})/(n^{\text{up}} + n^{\text{dn}})$ where n^{up} is the spin-up and n^{dn} is the spin-down electron density in a specific energy interval with respect to the Fermi energy E_F [E , E_F].
- [34] Two of the Fe atoms (denoted as Fe1) are directly below two carbon atoms while the other two (denoted as Fe2) are under a C=C double bond. This leads to a slightly different Fe—C interaction reflected by slightly different magnetic moments for the Fe1 and Fe2 atoms as well as exchange constants J describing the magnetic interactions between the nearest neighbor Fe—Fe atoms.
- [35] The lower ring binds to the substrate by chemical bonds and consequently, broad spin-polarized hybrid molecule-surface bands are formed. In contrast, the PDOS for the upper ring shows distinct sharp spin-split molecularlike features.